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FORM PTO-1390 (REV. 9-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 017769-000600US	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (if known, see 37 CFR 1.5) <b>10/030036</b>	
INTERNATIONAL APPLICATION NO. PCT/EP00/06350		INTERNATIONAL FILING DATE 04/07/00		PRIORITY DATE CLAIMED 05/07/99	
TITLE OF INVENTION TANDEM CELL FOR WATER CLEAVAGE BY VISIBLE LIGHT					
APPLICANT(S) FOR DO/EO/US Michel Grätzel, Jan Augustynski					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST submission of items concerning a filing under 35 U.S.C. 371.</b></p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 36 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 37(c)(2))</p> <p>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>a. <input checked="" type="checkbox"/> is attached hereto.</p> <p>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input checked="" type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p><b>Items 11 to 20 below concern document(s) or information included:</b></p> <p>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 36 U.S.C.</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information: International Search Report, ADS,</p>					

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US/ Application no (if known) <b>10/030036</b>		INTERNATIONAL APPLICATION NO <b>PCT/EP00/06350</b>		ATTORNEY'S DOCKET NUMBER <b>017769-000600US</b>	
21. <input checked="" type="checkbox"/> The following fees are submitted:				<b>CALCULATIONS PTO USE ONLY</b>	
<b>BASIC NATIONAL FEE (37 CFR 1.492(A) (1) - (5)):</b>					
Neither international preliminary examination fee (37 CFR 1.492) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .....				\$1040.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search report prepared by the EPO of JPO .....				\$890.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....				\$740.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....				\$710.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)(4) .....				\$100.00	
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				\$890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	8 - 20 =		x \$18.00	\$	
Independent claims	1 - 3 =		x \$84.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ 280.00	\$	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	
<b>SUBTOTAL =</b>				\$	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFT 1.492(f)).				\$	
<b>TOTAL NATIONAL FEE =</b>				\$	
Fee for recording the enclosed assignment (37 CFR 1.2(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
<b>TOTAL FEES ENCLOSED =</b>				\$890.00	
				Amount to be refunded: \$	
				charged: \$	
a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>20-1430</u> in the amount of \$ <u>890.00</u> to cover the above fees. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>20-1430</u> . A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. <b>Credit card information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.					
<b>NOTE:</b> Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:  J. Georg Seka Townsend and Townsend and Crew, LLP Two Embarcadero Center, Suite 800 San Francisco, CA. 94111-3834				SIGNATURE <u>J. Georg Seka</u> NAME  24,491 REGISTRATION NUMBER	
				01/03/02 DATE	

10/030036  
531 Rec'd PCT/PTO 03 JAN 2002

Attorney Docket No. 017769-000600US  
Client Reference No.: TACEL 6 209 PC

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re U.S. National Phase of:  
PCT/EP00/06350

Michel Graetzel, et al.

Application No.: Not yet assigned

Filed: Herewith

For: TANDEM CELL FOR WATER  
CLEAVAGE BY VISIBLE LIGHT

PRELIMINARY AMENDMENT

San Francisco, CA 94111  
January 3, 2002

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to the examination of the above-referenced application, please enter the following amendments and remarks.

IN THE ABSTRACT:

Please substitute the following amended, clean version of the Abstract (a marked-up version of the changes to the Abstract is attached to this Amendment):

**TANDEM CELL FOR WATER CLEAVAGE BY VISIBLE LIGHT**

**ABSTRACT OF THE DISCLOSURE**

The tandem cell or photoelectrochemical system for the cleavage of water to hydrogen and oxygen by visible light consisting of two superimposed photocells, both cells being connected electrically. The photoactive material in the top cell is a semiconducting oxide placed in contact with an aqueous solution. This semiconducting oxide absorbs the blue and green part of the solar emission spectrum of a light source or light sources and generates with the energy collected oxygen and protons from water. The not absorbed yellow and red light transmits the top cell and enters a second photocell, the bottom cell, which is mounted, in the direction of the light behind, preferably directly behind the top cell. The bottom cell includes a dye sensitized mesoporous photovoltaic film. The bottom cell converts the yellow, red and near infrared portion of the sunlight to drive the reduction of the protons which are produced in the top cell during the photo catalytic water oxidation process, to hydrogen.

IN THE CLAIMS:

Please substitute the following amended, clean versions of the indicated claims (a marked-up version of the changes to the claims is attached to this Amendment):

3. (amended) A photoelectrochemical system according to claim 1, characterized in that the photoactive oxide material present in the top cell is a doped form of  $\text{Fe}_2\text{O}_3$ , the dopant being selected from the elements Si, Ge, Sn, Pb, Ti, Zr, Hf, Sb, Bi, V, Nb, Ta, Mo, Tc, and Re or F, Cl, Br and I.
4. (amended) A photoelectrochemical system according to claim 1, characterized in that the photoactive  $\text{Fe}_2\text{O}_3$  in the doped or undoped form is present as a smooth layer, said layer having a thickness between 50 nm and 5000 nm said layer transmitting light of wavelength above 600 nm.
5. (amended) A photo electrochemical system according to claim 1, characterized in that the sensitizer is a ruthenium polypyridyl complex chosen from  $\text{RuL}_2(\text{NCS})_2$  and  $\text{RuL}'(\text{NCS})_3$ , where  $\text{L} = 4,4'$ -dicarboxy-2,2'-bipyridine and  $\text{L}' = 4,4'$ -tricarboxy-2,2',6',2''-terpyridine.
6. (amended) A photoelectrochemical system according to claim 1, characterized in that the oxygen and hydrogen evolution reaction take place both in the top cell and/or in separated compartments, said compartments being connected by an ion conducting membrane or a glass frit.
7. (amended) A photoelectrochemical system according to claim 1, characterized in that the hydrogen evolution is catalyzed by a metal, chosen from Ni, Pt, Pd, Ru, Rh and Ir, or alternatively by a polyacid or heteropolyacid chosen from tungsten, vanadium and molybdenum, said catalyst being deposited in the form of a thin coating on the cathode of the cell.
8. (amended) A photoelectrochemical system according to claim 1, characterized in that seawater is used as a source for hydrogen and oxygen in the water cleavage or water splitting device.

Michel Graetzel  
Application No. Not yet assigned  
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REMARKS:

Claims 1-8 are pending.

Amendment is made to delete a minor informality in the Abstract, and to eliminate all multiple dependencies from the claims, thereby avoiding the need to pay the multiple dependent surcharge.

Respectfully submitted,

  
J. Georg Seka  
Reg. No. 24,491

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**MARKED-UP VERSION OF THE CHANGES TO THE ABSTRACT**

[Abstract] ABSTRACT OF THE DISCLOURE

The tandem cell or photoelectrochemical system for the cleavage of water to hydrogen and oxygen by visible light consisting of two superimposed photocells, both cells being connected electrically. The photoactive material in the top cell is a semiconducting oxide placed in contact with an aqueous solution. This semiconducting oxide absorbs the blue and green part of the solar emission spectrum of a light source or light sources and generates with the energy collected oxygen and protons from water. The not absorbed yellow and red light transmits the top cell and enters a second photocell, the bottom cell, which is mounted, in the direction of the light behind, preferably directly behind the top cell. The bottom cell includes a dye sensitized mesoporous photovoltaic film. The bottom cell converts the yellow, red and near infrared portion of the sunlight to drive the reduction of the protons which are produced in the top cell during the photo catalytic water oxidation process, to hydrogen.

[(Fig. 1)]

### MARKED-UP VERSION OF THE CHANGES TO THE CLAIMS

3. (amended) A photoelectrochemical system according to [claim 1 or 2] claim 1, characterized in that the photoactive oxide material present in the top cell is a doped form of  $\text{Fe}_2\text{O}_3$ , the dopant being selected from the elements Si, Ge, Sn, Pb, Ti, Zr, Hf, Sb, Bi, V, Nb, Ta, Mo, Tc, and Re or F, Cl, Br and I.

4. (amended) A photoelectrochemical system according to [claim any of claims 1 to 3] claim 1, characterized in that the photoactive  $\text{Fe}_2\text{O}_3$  in the doped or undoped form is present as a smooth layer, said layer having a thickness between 50 nm and 5000 nm said layer transmitting light of wavelength above 600 nm.

5. (amended) A photo electrochemical system according to [any of claims 1-4] claim 1, characterized in that the sensitizer is a ruthenium polypyridyl complex chosen from  $\text{RuL}_2(\text{NCS})_2$  and  $\text{RuL}'(\text{NCS})_3$ , where  $\text{L} = 4,4'$ -dicarboxy-2,2'-bipyridine and  $\text{L}' = 4,4'4''$ -tricarboxy-2,2',6',2''-terpyridine.

6. (amended) A photoelectrochemical system according to [any of claims 1-5] claim 1, characterized in that the oxygen and hydrogen evolution reaction take place both in the top cell and/or in separated compartments, said compartments being connected by an ion conducting membrane or a glass frit.

7. (amended) A photoelectrochemical system according to [any of claims 1-6] claim 1, characterized in that the hydrogen evolution is catalyzed by a metal, chosen from Ni, Pt, Pd, Ru, Rh and Ir, or alternatively by a polyacid or heteropolyacid chosen from tungsten, vanadium and molybdenum, said catalyst being deposited in the form of a thin coating on the cathode of the cell.

8. (amended) A photoelectrochemical system according to [any of claims 1-7] claim 1, characterized in that seawater is used as a source for hydrogen and oxygen in the water cleavage or water splitting device.

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TACEL 6 209 PCT

École Polytechnique Fédérale de Lausanne, SRI, CH-1015 Lausanne, Suisse

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TANDEM CELL FOR WATER CLEAVAGE BY VISIBLE LIGHT

The invention is related to a photoelectrochemical system for the cleavage of water to hydrogen and oxygen according to the preamble of the independent claim 1.

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Previous systems that accomplish the direct splitting of water by visible light with a comparably high efficiency employ very expensive single crystal semiconductor materials. For details see O.Khaselev and J.Turner, Science 280, 1998, 455).

Therefore these previous systems are not suitable for practical applications to produce hydrogen and oxygen from sunlight.

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According to the invention a photoelectrochemical system is characterized by the features of the characterizing part of the independent claim 1. The depending claims are related to particularly favorable embodiments of the invention. The improved photoelectrochemical system provides for photoelectrochemical tandem cells that show

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a considerably high efficiency. Further the photoelectrochemical system can be manufactured at relatively low cost. A further advantage of the present invention is that seawater can be used for the process instead of pure water.



Description of the invention, device structure.

In the following the invention will now be described by way of example and with  
5 reference to the accompanying drawings that show the following:

Fig. 1 shows a schematic drawing of the water photolysis device that is the  
object of the present invention.

10 Fig. 2 shows the spectral dependency of the photon-to electric current  
conversion achieved with the sensitized  $\text{TiO}_2$  films for several  
ruthenium complexes; it shows the incident photon to current  
conversion efficiencies obtained with various sensitizer;

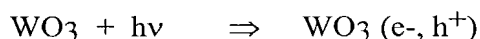
15 Fig. 3 shows an energy level diagram that illustrates the functioning of the  
tandem cell; it shows the Z scheme of biphotonic water photolysis

A schematic representation of the water photolysis device, that is the object of the  
present invention is described is illustrated in Fig. 1. The device consists of two photo  
20 systems connected in series. The cell on the left contains the aqueous electrolyte that is  
subjected to water photolysis. The electrolyte is composed of water as a solvent to  
which an electrolyte has been added for ionic conduction. Saline seawater can also be  
used as a water source in which case the addition of electrolyte becomes superfluous.  
Light enters from the left side of the cell through a glass window (1). After traversing  
25 the electrolyte (2) it impinges on the back wall of the cell constituted by a mesoporous  
semiconductor film composed of an oxide such as  $\text{WO}_3$  or  $\text{Fe}_2\text{O}_3$  (3), The latter is  
deposited onto a transparent conducting oxide film (4), made from a material such as  
fluorine doped tin dioxide that serves as current collector which is deposited on the  
glass sheet (1). The oxide absorbs the blue and green part of the solar spectrum while  
30 the yellow and red light is transmitted through it. The yellow and red part of the solar  
spectrum is captured by a second cell mounted behind the back wall of the first cell.  
The second cell contains a dye sensitized mesoporous  $\text{TiO}_2$  film. Its functions as a

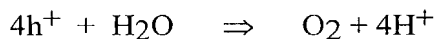
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light driven electric bias increasing the electrochemical potential of the electrons that emerge from the WO<sub>3</sub> film under illumination to render the reduction of water to hydrogen possible. It consists of a transparent conducting oxide film (4) deposited on the back side of the glass sheet (1) constituting the back wall of the first cell. The conducting oxide film is covered by the dye-derivatized nanocrystalline titania film (6). The latter is in contact with the organic redox electrolyte (7) and the counter electrode (8) consisting of a glass which is rendered conductive on the side of the organic electrolyte by deposition of a transparent conductive oxide layer. Behind the counterelectrode there is a second compartment (9) containing an aqueous electrolyte of the same composition as in the front compartment (2). Hydrogen is evolved at the cathode (10) which is immersed in this second electrolyte compartment. The two electrolyte compartments (2) and (10) have the same composition and are separated by an ion conducting membrane or a glass frit (11).

We shall now discuss a specific embodiment of such a tandem device achieving the direct cleavage of water into hydrogen and oxygen by visible light. A thin film of nanocrystalline tungsten trioxide absorbs the blue part of the solar spectrum.



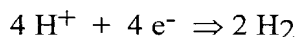
The valence band holes (h<sup>+</sup>) created by band gap excitation of the oxide serve to oxidize water forming oxygen and protons:



while the conduction band electrons are collected on the conducting glass support forming the back wall of the first photocell. From there on they are fed into the second photocell that consists of a dye sensitized nanocrystalline TiO<sub>2</sub> film. The latter is mounted directly behind the WO<sub>3</sub> film capturing the green and red part of the solar spectrum that is transmitted through the top electrode. The role of the second photocell is merely that of a photo driven bias. The electrochemical potential of the electrons is

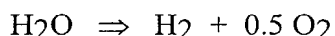
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sufficiently increased by passing through the second photocell that they can reduce the protons produced during water oxidation to hydrogen.



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The overall reaction corresponds to the splitting of water by visible light.



Semiconducting oxides, such as  $\text{WO}_3$  and  $\text{Fe}_2\text{O}_3$  are the materials of choice for the photo-anode as they are stable under operation resisting to both dark and photo corrosion. Tungsten trioxide and ferric oxide are so far the only known and readily available oxide semiconductors that are capable of producing oxygen using visible light. The electrons generated in the oxide are collected by the conducting glass and are subsequently fed into a second photocell that is placed directly behind the oxide film.

The photo-active element of this second cell is a dye sensitized mesoporous  $\text{TiO}_2$  capturing the yellow and red light that is transmitted through the oxide electrode. It serves as a photo- driven bias increasing the electrochemical potential of the photoelectrons produced by band gap excitation of the oxide to render reduction of water to hydrogen feasible.

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Fig. 2 presents the spectral dependency of the photon-to electric current conversion achieved with the sensitized  $\text{TiO}_2$  films for several ruthenium complexes. Very high efficiencies of current generation, exceeding 75% are obtained. When corrected for the inevitable reflection and absorption losses in the conducting glass that serves to support the film the yields are practically 100 percent. For the dyes  $\text{RuL}_2(\text{SCN})_2$  and  $\text{RuL}'(\text{SCN})_3$  the photo-response of the film extends well into the red and near infrared part of the spectrum making these complexes an appropriate choice for the harvesting of the red and yellow part of sun light by the second photocell in the tandem system .

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The functioning of the tandem cell is further illustrated by the energy level diagram shown in Fig. 3. There is close analogy to the Z-scheme operative in the light reaction in green plants in which the two photo systems are connected in series, one affording

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oxidation of water to oxygen and the other generating the NADPH used in CO<sub>2</sub> fixation. At this stage of development the overall AM 1.5 solar light to chemical conversion efficiency achieved stands at 5 %.

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#### Working Example

The preparation of transparent mesoporous WO<sub>3</sub> films of a few micron thickness has been achieved via a sol-gel type process. A colloidal WO<sub>3</sub> precursor solution was  
10 prepared first and after mixing with polyvinyl alcohol, films were deposited on conducting glass (Nippon Sheet Glass, 10 ohm/o, fluorine-doped SnO<sub>2</sub> glass (TCO)) surface. In order to supply the bias necessary to reach the plateau photocurrent, two in series connected sensitized mesoporous TiO<sub>2</sub> injection cells were placed under the transparent WO<sub>3</sub> film. This configuration reached a photocurrent of 3.5 mA/cm<sup>2</sup> for  
15 hydrogen generation in simulated AM 1.5 sunlight. This corresponds to an overall solar to chemical conversion efficiency of 5 % for light induced water cleavage by AM 1.5 standard sunlight.

This example illustrates the successful operation of the tandem device which is the  
20 object of the present invention. It is based on two superimposed photocells having complementary light absorption in the visible and near infrared range according to the embodiment described in the patent disclosure. Such a tandem cell accomplishes the splitting of water into hydrogen and oxygen by visible light directly rendering the use of a separate electrolysis cell superfluous. Thus it is preferred over alternative systems  
25 where traditional photovoltaic cells, such as silicon solar cells are used in conjunction with a water electrolyzer. The present invention renders the water electrolyzer superfluous reducing the cost of the water splitting device substantially. Apart from the cost there it is also advantageous from the operational point of view. In the conventional photoelectrolysis systems based on the combination of silicon solar cells  
30 with a water electrolyzer, several photovoltaic cells have to be connected in series to yield the voltage of about 1.7 V required for the operation of the water electrolyzer. Furthermore each of the photovoltaic cells should operate at its optimum power point

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to keep losses low and the efficiency high. However as the power point fluctuates according to the intensity and spectral distribution of the incident solar radiation one needs to install a very complicated system that changes the number of in series connected cells in response to the meteorological conditions. This renders the system expensive and its operation complex. In contrast the tandem cell described by the present invention operates at practically the same efficiency irrespective of the intensity and spectral distribution of the incident solar light.

The additional advantage of the present invention is that it uses low cost materials, the semiconductor layers employed being made from cheap and readily available oxide films having a mesoporous morphology. The tandem cell exhibits an overall conversion efficiency of 5 % for the photo cleavage of water into hydrogen and oxygen.

A further advantage of the present invention is that seawater can be employed instead of pure water. The salt contained in seawater produces the ionic conductivity required for operating the water cleavage device. This saves the cost for desalination of the water and for providing the electrolyte supplement which is required if pure water is employed in the electrolyzer.

The invention relates to a tandem device based on two superimposed photocells having complementary light absorption in the visible and near infrared range. Such a tandem cell accomplishes the splitting of water into hydrogen and oxygen by visible light directly rendering the use of a separate electrolysis cell superfluous. The additional advantage of the present invention is that it uses low cost materials, the semiconductor layers employed being made from cheap and readily available oxide films having a mesoporous morphology. The tandem cell exhibits an overall conversion efficiency of 5 % for the photo cleavage of water into hydrogen and oxygen.

The tandem cell or photoelectrochemical system for the cleavage of water to hydrogen and oxygen by visible light consisting of two superimposed photocells, both cells being connected electrically. The photoactive material in the top cell is a semiconducting oxide placed in contact with an aqueous solution. This semiconducting oxide absorbs

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the blue and green part of the solar emission spectrum of a light source or light sources and generates with the energy collected oxygen and protons from water. The not absorbed yellow and red light transmits the top cell and enters a second photocell, the bottom cell, which is mounted, in the direction of the light behind, preferably directly

5 behind the top cell. The bottom cell includes a dye sensitized mesoporous photovoltaic film. The bottom cell converts the yellow, red and near infrared portion of the sunlight to drive the reduction of the protons which are produced in the top cell during the photo catalytic water oxidation process, to hydrogen.

10 Although the use of the photoelectrochemical system with the tandem cell according to the invention can be most advantageously used with sun light, it can be driven with the light of any light source or light sources that emit light of the required frequencies.

15 The reference numbers used in Fig. 1 denominate the following:

- 1 Glass sheet
- 2 Aqueous electrolyte
- 20 3 Mesoporous oxide film, e.g.,  $\text{WO}_3$   $\text{Fe}_2\text{O}_3$
- 4 Transparent conducting oxide (TCO) film
- 5 Electrical connection
- 25 6 Dye sensitized mesoporous  $\text{TiO}_2$  film
- 7 Organic redox electrolyte for dye sensitized solar cell (DYSC), used in tandem
- 30 8 Counter electrode for DYSC
- 9 Aqueous electrolyte (same composition as 2)
- 10 Catalytic cathode for  $\text{H}_2$  evolution
- 35 11 Glass frit

## Claims

1. A photoelectrochemical system for the cleavage of water to hydrogen and oxygen by visible light consisting of two superimposed photocells, both cells  
5 being connected electrically, characterized in that the photoactive material in the top cell is a semiconducting oxide placed in contact with an aqueous solution, said oxide absorbing the blue and green part of the solar emission spectrum to generate oxygen and protons from water and transmitting the yellow and red light to a second photocell mounted behind the top cell and composed of a dye  
10 sensitized mesoporous photovoltaic film, said bottom cell converting the yellow, red and near infrared portion of the sunlight to drive the reduction of the protons, produced in the top cell during the photo catalytic water oxidation process, to hydrogen.
- 15 2. A photoelectrochemical system for the direct cleavage of water to hydrogen and oxygen by visible light according to claim 1, consisting of two superimposed photocells, both cells being connected electrically, wherein the photoactive material present in the top photocell is a thin film of  $\text{WO}_3$  or  $\text{Fe}_2\text{O}_3$  deposited  
20 on a conducting substrate or conducting glass and placed in contact with an aqueous electrolyte solution, said  $\text{WO}_3$  tungsten oxide or  $\text{Fe}_2\text{O}_3$  iron oxide absorbing the blue and green part of the solar emission spectrum to generate oxygen and protons from water and transmitting the yellow and red light to a bottom photocell mounted behind the top photocell and composed of a dye  
25 sensitized photovoltaic film, said second photocell converting the yellow, red and near infrared portion of the solar emission spectrum to drive the reduction of the protons, produced in the top photocell during the water oxidation process, said reduction of protons to hydrogen gas taking place in an electrolyte compartment mounted behind the bottom photocell and being separated from  
30 the top photocell compartment where oxygen is evolved by a glass frit or an ion conducting membrane.

- 9 -

3. A photoelectrochemical system according to claim 1 or 2, characterized in that the photoactive oxide material present in the top cell is a doped form of  $\text{Fe}_2\text{O}_3$ , the dopant being selected from the elements Si, Ge, Sn, Pb, Ti, Zr, Hf, Sb, Bi, V, Nb, Ta, Mo, Tc, and Re or F, Cl, Br and I.

5

4. A photoelectrochemical system according to claim any of claims 1 to 3, characterized in that the photoactive  $\text{Fe}_2\text{O}_3$  in the doped or undoped form is present as a smooth layer, said layer having a thickness between 50 nm and 5000 nm said layer transmitting light of wavelength above 600 nm.

10

5. A photoelectrochemical system according to any of claims 1- 4, characterized in that the sensitizer is a ruthenium polypyridyl complex chosen from  $\text{RuL}_2(\text{NCS})_2$  and  $\text{RuL}'(\text{NCS})_3$ , where  $\text{L} = 4,4'$ -dicarboxy-2,2'-bipyridine and  $\text{L}' = 4,4'4''$ -tricarboxy-2,2',6',2''-terpyridine.

15

6. A photoelectrochemical system according to any of claims 1-5, characterized in that the oxygen and hydrogen evolution reaction take place both in the top cell and/or in separated compartments, said compartments being connected by an ion conducting membrane or a glass frit.

20

7. A photoelectrochemical system according to any of claims 1 –6, characterized in that the hydrogen evolution is catalyzed by a metal, chosen from Ni, Pt, Pd, Ru, Rh and Ir ,or alternatively by a polyacid or heteropolyacid chosen from tungsten, vanadium and molybdenum., said catalyst being deposited in the form of a thin coating on the cathode of the cell.

25

8. A photoelectrochemical system according to any of claims 1-7, characterized in that seawater is used as a source for hydrogen and oxygen in the water cleavage or water splitting device.

30



- 10 -

## Abstract

10/030036

The tandem cell or photoelectrochemical system for the cleavage of water to hydrogen and oxygen by visible light consisting of two superimposed photocells, both cells being  
5 connected electrically. The photoactive material in the top cell is a semiconducting oxide placed in contact with an aqueous solution. This semiconducting oxide absorbs the blue and green part of the solar emission spectrum of a light source or light sources and generates with the energy collected oxygen and protons from water. The not  
10 absorbed yellow and red light transmits the top cell and enters a second photocell, the bottom cell, which is mounted, in the direction of the light behind, preferably directly behind the top cell. The bottom cell includes a dye sensitized mesoporous photovoltaic film. The bottom cell converts the yellow, red and near infrared portion of the sunlight to drive the reduction of the protons which are produced in the top cell during the photo  
15 catalytic water oxidation process, to hydrogen.

(Fig. 1)

1 / 3

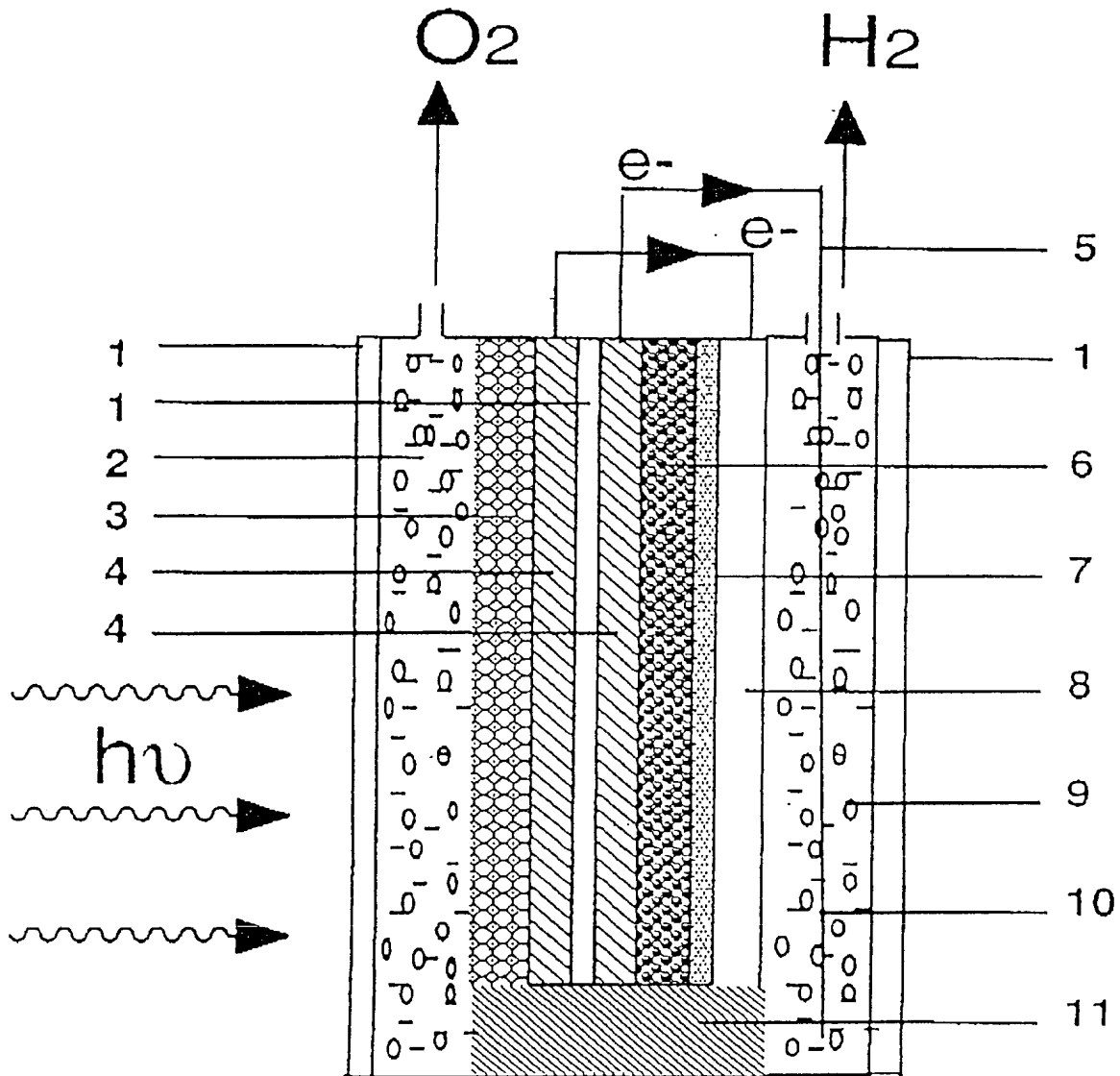
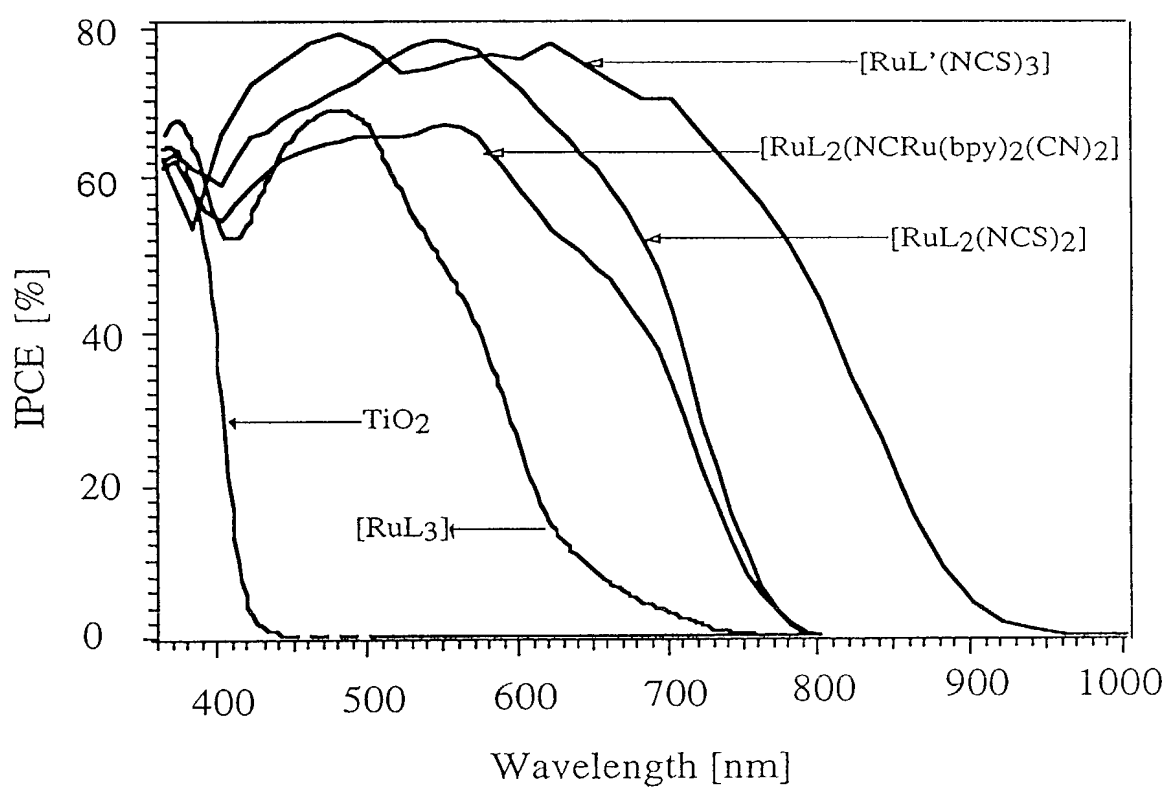


Fig. 1

2 / 3

Incident Photon to Current Conversion  
Efficiencies Obtained with Various Sensitizers



$L' = 4,4',4''$ -tricarboxy-2,2', 6',2''-terpyridine

$L = 4,4'$ -dicarboxy-2,2'-bipyridine

Fig. 2

## The Z scheme of biphotonic water photolysis

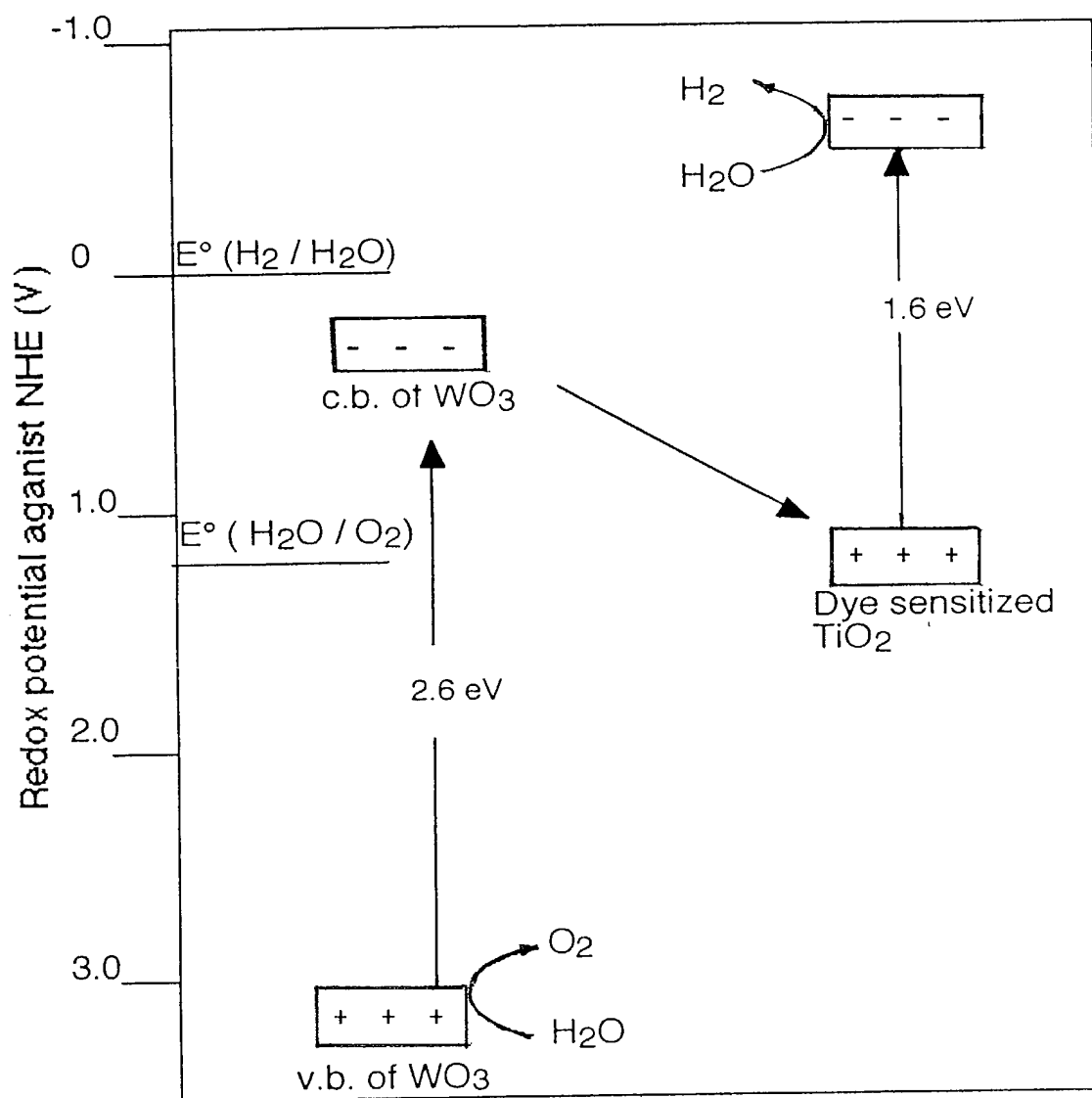


Fig. 3

**DECLARATION FOR UTILITY OR  
DESIGN  
PATENT APPLICATION  
(37 CFR 1.63)**

☐ Declaration  
Submitted  
With Initial  
Filing

OR

☐ Declaration  
Submitted after Initial  
Filing (surcharge  
(37 CFR 1.16(e))  
required)

Attorney Docket Number

017769-000600US

First Named Inventor

Michel Graetzel, et al.

**COMPLETE IF KNOWN**

Application Number

10/030,036

Filing Date

10/30/02

Art Unit

Examiner Name

As the below named inventor, I hereby declare that:

My residence, mailing address, and citizenship are as stated below next to my name

I believe I am the original and first inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled

**TANDEM CELL FOR WATER CLEAVAGE BY VISIBLE LIGHT**

the specification of which

(Title of the Invention)

☐ is attached hereto

OR

☐ was filed on (MM/DD/YYYY)

as United States Application Number or PCT International

Application Number

Not yet assigned

and was amended on (MM/DD/YYYY)

(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
				YES	NO
PCT/EP00/06350 99810592 8	PCT	July 4, 2000	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	EP	July 5, 1999	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
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☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto

[Page 1 of 2]

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<b>POWER OF ATTORNEY OR AUTHORIZATION OF AGENT</b>	<b>Application Number</b>	10/030,036
	<b>Filing Date</b>	
	<b>First Named Inventor</b>	Grätzel Michael
	<b>Title</b>	Tandem Cell for Water Cleavage by Visible Light
	<b>Group Art Unit</b>	
	<b>Examiner Name</b>	
	<b>Attorney Docket Number</b>	117769-0006000US

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☒ Applicant/Inventor

☐ Assignee of record of the entire interest See 37 CFR 3.71  
 Statement under 37 CFR 3.73(b) is enclosed (Form PTO/SB/96)
**SIGNATURE of Applicant or Assignee of Record**

Name	Jan Augustynski	Michael Gratzel
Signature		
Date	Datum 7.2.2002	Datum 3.2.2002

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below\*

☒ \*Total of 1 forms are submitted.

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☐ Additional inventors are being named on the \_\_\_\_\_ supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto

## DECLARATION

## ADDITIONAL INVENTOR(S)

## Supplemental Sheet

Page 3 of 3

2-00  
Name of Additional Joint Inventor, if any:☐ A petition has been filed for this unsigned inventor

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